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Flash Photolysis of Some Photochromic N-Benzylideneanilines

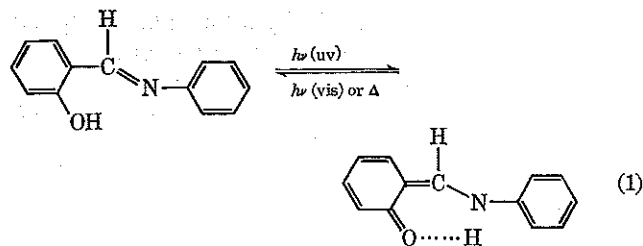
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The flash photolysis of dilute (10^{-4} M) oxygen-free solutions of *o*-carboxy- (I), *o*-methyl- (II), *o*-nitro- (III), and *o*-aminobenzylideneanilines (IV) in polar and nonpolar solvents has been investigated. Intense, colored transients are produced in the wavelength region 410–470 nm. For compounds I, II, and IV, the transients have been attributed to quinoid-type isomers formed through an intramolecular hydrogen transfer from the *o*-substituent to the nitrogen of the $>C=N-$ group. For compound III, the quinoid isomer is tentatively suggested to be produced from an intermediate H atom adduct on the nitro group. Kinetic data are reported for the thermal decay of the different transients formed. The results are compared with those obtained for salicylideneanilines. This work indicates that the transient photochromic band may arise from an *ortho* group other than *o*-OH, provided that this group is capable of transferring a hydrogen atom to the nitrogen of the $>C=N-$ group.

Introduction

In the crystalline state, salicylideneaniline and its derivatives (called "anils") undergo reversible color changes induced by light and by heat, with the formation of an absorption band in the visible region (maximum around 480 nm). This process can be reversed, *i.e.*, bleaching occurs, on irradiation with light absorbed by the new band or thermally in the dark. This color-deepening endows these molecules with their photochromic properties. Cohen and Schmidt^{2,3} showed that any one anil crystalline form can be either photochromic or thermochromic, but not both. In rigid solutions these compounds are photochromic, and they concluded^{2,3} that photochromism is an intrinsic property of the individual anil molecule rather than a result of molecular interactions in the crystal. The hydroxyl group in an *ortho* position was considered^{2,3} an essential condition for this phenomenon, and it was proposed² that the action of light upon the anils causes a hydrogen atom transfer to form a keto anil.



Using flash photolysis techniques, it was found⁴ that the absorption band around 480 nm, typical of photochromic anils, arises also in solutions at room temperature and disappears with a lifetime in the millisecond

(1) Visiting scientist from the Nuclear Research Center "Democritos," Athens, Greece.

(2) M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, **66**, 2442 (1962).

(3) M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, *J. Chem. Soc.*, 2051, 2060 (1964).

(4) G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, **40**, 1486 (1964).

region. More recent works,⁵⁻⁸ on the mechanism of photochromic anils, attempted a more detailed study of the electronic absorption and emission spectra of these compounds to evaluate the nature of the precursors of the photoinduced colored intermediate. While progress has been made, the mechanism leading to this photo-coloration is not yet understood. For example, the statement that the *o*-OH group is an essential condition for photochromism² has been criticized by some investigators. Becker and Richey⁶ reported that several nitrosalicylaldehyde derivatives do not show this phenomenon, while Osipov, *et al.*,⁹ claim that the *o*-OH group is not a determining condition for the development of color and that *o*-nitrobenzylideneaniline has been reported¹⁰ as being photochromic in the crystalline state.

In an attempt to clarify the role of the *o*-hydroxyl group, we have studied compounds with *ortho* derivatives other than OH groups using the technique of flash photolysis together with spectroscopic and esr observations. The *o*-carboxy, *o*-methyl, *o*-nitro, and *o*-amino derivatives of benzylideneaniline were examined. These compounds have not been previously studied using flash photolysis techniques.

Experimental Section

The compounds used in this work were prepared from the condensation of the *o*-substituted benzaldehydes with aniline. Melting points, ir and nmr spectroscopy, and chromatography were utilized to establish the purity of the compounds. All the solvents used were Spectrograde from Eastman or Matheson Coleman and Bell, except ethanol which was U.S.I. absolute alcohol. The flash photolysis lamps and experimental setup used in this work have been described elsewhere.¹¹ The optical absorption spectra of the transient species, produced in 20-cm optical cells, were obtained by the point-by-point method. Reaction rate constants were determined using a computer by least-squares approximation of first- and second-order reactions. All the spectra reported were obtained in degassed solutions (flushing for 1 hr with prepurified nitrogen), and a fresh solution was used for each flash. Absorption spectra were taken on a Cary 11 recording spectrophotometer. A quartz Dewar vessel with quartz windows was used for the measurement of optical spectra in rigid glasses at low temperature.

Esr spectra were taken¹² by irradiating the specimen within the microwave cavity (Varian V-4500 with 100-kc field modulation) or immediately after one flash, in the flash photolysis setup, and then transferred to the cavity. The sensitivity of the spectrometer was frequently checked with a sample of DPPH. The rates of disappearance of the radical were determined by following the decrease of the esr signal with time.

Results

Flash Photolysis of o-Carboxy- (I) and *o*-Methylbenzylideneaniline (II). On exposing a 10^{-4} M oxygen-

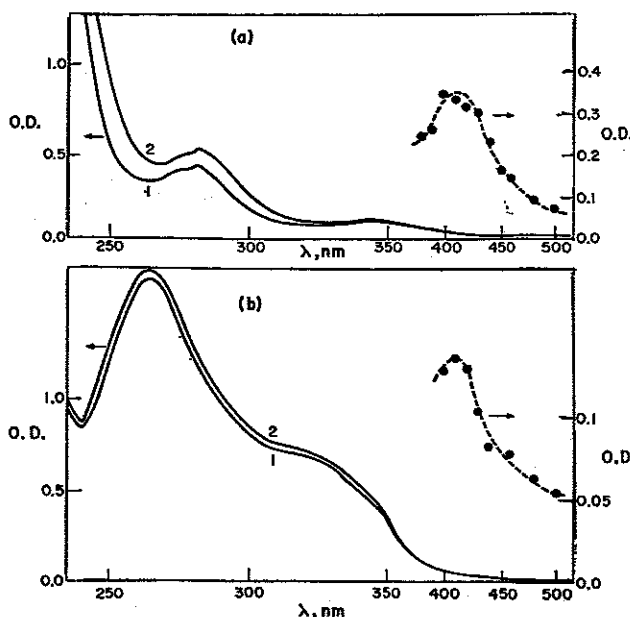


Figure 1. (a) Spectral changes produced on flash photolysis of 10^{-4} M *o*-carboxybenzylideneaniline in ethanol: ●, transient absorption spectrum, OD measured 60 μ sec after start of flash; absorption spectrum of solution measured before (1) and after (2) the flash. (b) Spectral changes produced on flash photolysis of 10^{-4} M *o*-methylbenzylideneaniline in heptane: ●, transient absorption spectrum, OD read at 300 μ sec after start of flash; absorption spectrum of solution measured before (1) and after (2) the flash.

free solution of I or II in ethanol or heptane to a high-intensity pulse of uv light, a new absorption band with a maximum at ~ 410 nm is observed (see Figure 1). This band disappears with a lifetime in the millisecond range in ethanol and approximately 500 times slower in heptane. In both cases, a residual permanent absorption is also observed indicating the formation of a permanent photoproduct. Repeated flashings, or steady-state illumination with uv light, of these solutions results in small spectral changes, indicating that most of the change takes place in the first flash. The kinetics of the fading of these transient species in ethanol followed second-order decay, with rate constants $2k/\epsilon$ of 5.3×10^5 and 3.9×10^4 cm sec⁻¹ for I and II, respectively. In air-saturated solutions (1 atm) the intensity of the transient formed is reduced by $\sim 15\%$.

(5) M. Ottolenghi and D. S. McClure, *J. Chem. Phys.*, **46**, 4613, 4620 (1967).

(6) R. S. Becker and W. F. Richey, *J. Amer. Chem. Soc.*, **89**, 1298 (1967).

(7) W. F. Richey and R. S. Becker, *J. Chem. Phys.*, **49**, 2092 (1968).

(8) R. Potashnik and M. Ottolenghi, *ibid.*, **51**, 3671 (1969).

(9) O. A. Osipov, Yu. A. Zhdanov, M. I. Knyarhanskii, V. Z. Minkin, A. D. Garmovskii, and I. D. Sadkov, *Russ. J. Phys. Chem.*, **41**, 322 (1967).

(10) W. Borsche and F. Sell, *Chem. Ber.*, **83**, 78 (1950).

(11) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 2511 (1967); M. E. Langmuir and E. Hayon, *ibid.*, **71**, 3808 (1967).

(12) We thank Dr. M. Arick for making these measurements.

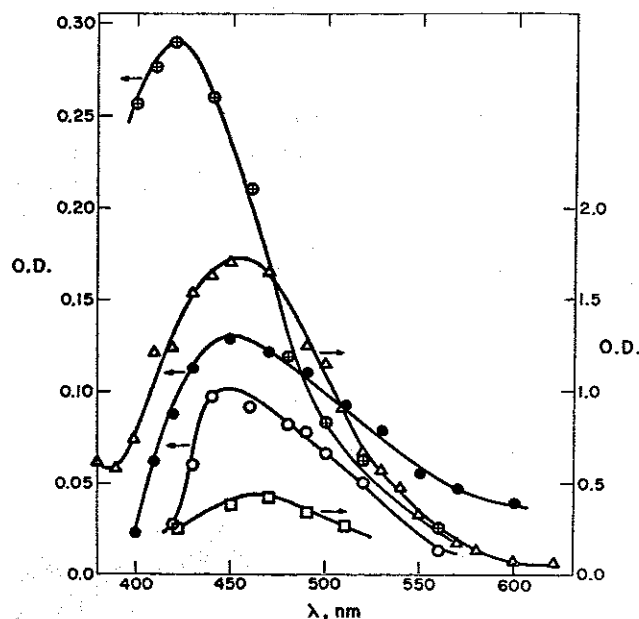


Figure 2. Visible absorption spectra of transients produced on flash photolysis of 10^{-4} M *o*-nitrobenzylideneaniline in heptane (Δ), benzene (\square), acetonitrile (\oplus), dimethylformamide (\bullet), and ethanol (\circ) solutions. OD's were measured at 2 msec after start of flash.

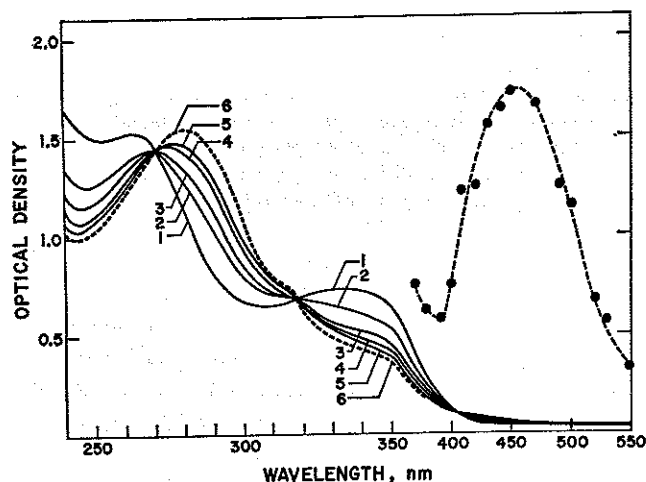


Figure 3. Spectral changes observed after flash photolysis of 10^{-4} M *o*-nitrobenzylideneaniline in heptane: spectrum 1 taken before flash and spectra 2-5 taken after 1 to 4 flashes on the same solution. Dotted line 6 is the absorption spectrum of *o*-nitrosobenzanilide in heptane. Symbols \bullet show transient spectrum produced on flash photolysis of 10^{-4} M *o*-nitrobenzylideneaniline in heptane; OD's were measured at 2 msec after start of flash.

Flash Photolysis of *o*-Nitrobenzylideneaniline (III). On flash photolysis of 10^{-4} M solutions of III in heptane, benzene, ethanol, dimethylformamide (DMF), and acetonitrile, a new absorption band is formed with maxima at ~ 455 nm in heptane, ~ 460 nm in benzene, ~ 450 nm in ethanol, ~ 445 nm in DMF, and ~ 425 nm in acetonitrile (see Figure 2). The intensity of the transient is stronger in heptane, and the relative

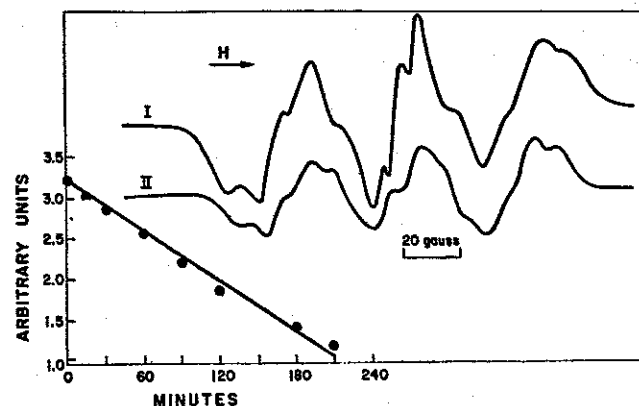


Figure 4. ESR spectra of radicals produced (I) from *o*-nitrobenzylideneaniline in THF in presence of Na metal at 22° , and (II) after flash photolysis of 2×10^{-3} M *o*-nitrobenzylideneaniline in heptane at 22° . Insert: plot of first-order decay of the photoradical followed in the esr cavity ($k = 1.6 \times 10^{-4} \text{ sec}^{-1}$).

sequence of intensity in the various solvents is heptane $>$ benzene $>$ acetonitrile $>$ DMF $>$ ethanol. In the three polar liquids, the new band is formed *immediately* after the flash and disappears with a lifetime in the millisecond region. In heptane and benzene the transient is produced slowly after the flash, builds up to a maximum absorption in ~ 8 msec, and then decays very slowly. The rates of formation appear to be neither first nor second order. The rates of decay in heptane and benzene followed first-order kinetics with $k \simeq 0.5 \text{ sec}^{-1}$. In ethanol, DMF, and acetonitrile, the decay kinetics were also first order with $k \simeq 2.2 \times 10^3 \text{ sec}^{-1}$.

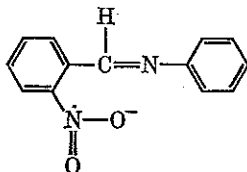
In air-saturated solutions (1 atm) the transient absorption is reduced by $\sim 15\%$ in these solvents.

Successive flashing or steady-state illumination from a high-pressure Hg lamp brings about permanent spectral changes, as shown in Figure 3. On irradiation of III in benzene solutions, Sachs and Kempf¹³ found an isomeric change with the formation of *o*-nitrosobenzanilide. This compound (mp 171°) is insoluble and precipitates as a white powder. It was prepared as described;¹³ its mp was verified and its absorption spectrum in heptane is displayed in Figure 3. A comparison of this spectrum with that formed on flashing, Figure 3, would seem to indicate the formation of *o*-nitrosobenzanilide as a permanent photoproduct.

All the solutions of III produce a long-lived free radical on exposure to one flash of light, as subsequently measured by esr spectroscopy. The esr spectrum of this radical in 2×10^{-3} M heptane solutions of III is shown in Figure 4. *In situ* photolysis in the esr cavity of a flowing solution of III in heptane did not show the presence of a second radical. A somewhat similar esr spectrum was also observed in solutions of III in tetrahydrofuran (THF) in presence of Na metal (Figure

(13) F. Sachs and R. Kempf, *Ber.*, **35**, 2704 (1902).

4). The observed radical is tentatively suggested to be the nitro-anion species



The decay of this radical in heptane at 22° follows first-order kinetics, with a rate constant $k = 1.6 \times 10^{-4} \text{ sec}^{-1}$ (see Figure 4). It should be mentioned that a long-lived free radical is also formed¹⁴ in the steady-state photolysis of compound III in the solid state, but in the absence of single crystal studies one cannot ascertain the similarity between the two species.

Flash Photolysis of *o*-Aminobenzylideneaniline (IV). Flash photolysis of $10^{-4} M$ solutions of IV in heptane or ethanol leads to the formation of three new absorption bands with λ_{max} at ~ 455 , 470, and 620 nm (see Figure 5). The bands at 470 and 620 nm disappear with a lifetime in the millisecond region, but the band at 455 nm decays about 20 times faster. The intensity of the 455-nm band is much stronger in heptane than in ethanol. The species responsible for the 455- and 620-nm bands decayed following second-order kinetics with $2k/\epsilon$ values of 2.0×10^6 and $3.4 \times 10^5 \text{ cm sec}^{-1}$, respectively, while the 470-nm band decayed by a first-order process with $k = 1.5 \times 10^3 \text{ sec}^{-1}$. Although a small residual permanent absorption was observed, the same solution was recycled at least 15 times without observing any further significant change, indicating that the photochemical reaction is essentially fully reversible under these experimental conditions.

In air-saturated solutions, the intensity of the 455-nm band is reduced by $\sim 30\%$ while the two other bands are reduced by $\sim 15\%$.

On photolysis of IV in EPA solvent at 77°K, a new absorption band with $\lambda_{\text{max}} \sim 610 \text{ nm}$ is formed (see Figure 5), which disappears on thawing the rigid glass to room temperature.

When compound IV is dissolved in concentrated sulfuric acid, an absorption band appears with a maximum at $\sim 470 \text{ nm}$. In the solid state, IV turns from yellow to red on reaction with H_2SO_4 , and the ir spectrum of the solid red compound in KBr shows the so-called¹⁵ "ammonium band" in the range 3000–2200 cm^{-1} .

Discussion

The data presented above show that a new absorption band in the region 410–470 nm appears on flash photolysis of compounds I–IV in different solvents, indicating the possibility of a common transient species. This band seems to be similar to the so-called photochromic band observed on flash photolysis^{4,8} of *o*-hydroxybenzylideneaniline (salicylideneaniline) or on photol-

ysis^{2,3} in rigid glasses or in the crystalline state. This band was attributed^{2,3} to the formation of a quinoid isomer, reaction 1. It thus seems probable that the transients observed above, which give rise to a similar band in the same wavelength region, are also of quinoid character. These bands do not correspond to possible *cis-trans* isomerizations, since such isomerizations produce changes¹⁶ in the spectrum at lower wavelengths, at about 370 nm.

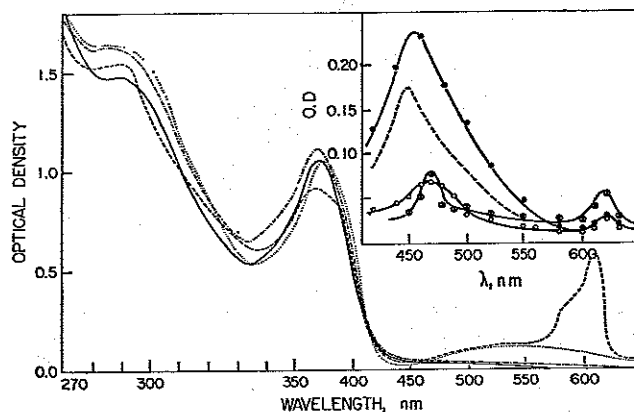


Figure 5. Absorption spectra of $10^{-4} M$ *o*-aminobenzylideneaniline in EPA measured at 22° (—), — 196° as a rigid glass (.....), photolysis of glass with Hg lamp for 30 min, — 196° as a rigid glass (---), photolyzed solution measured at 22° (----). Insert: transient spectra produced on flash photolysis of $10^{-4} M$ *o*-aminobenzylideneaniline in heptane: OD's were read at 40 (●) and 400 μsec (○) after flash, and dotted line is difference spectrum. In ethanol (⊙): OD's were measured at 400 μsec after flash.

For compounds I, II, and IV, the quinoid isomer can be produced by a mechanism similar to that suggested for salicylideneaniline, *i.e.*, a hydrogen transfer from the *ortho* group to the nitrogen atom of the C=N group. Compound III does not, however, have a hydrogen atom in the *ortho* position. It is suggested that *o*-nitrobenzylideneaniline initially forms an intermediate H atom adduct, $-\text{NO}_2\text{H}$, similar¹⁷ to the suggested photochemical rearrangement of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid. These experiments cannot distinguish between an intramolecular H atom transfer, or an H atom abstraction from the solvent by an electronically excited nitro group.

The *o*-aminobenzylideneaniline, in addition to the 455-nm band attributed to the quinoid isomer, presents two bands at 470 and 620 nm. These bands are tentatively suggested to be due to ionic species: (a) the

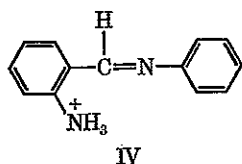
(14) E. Hadjoudis and E. Hayon, *J. Phys. Chem.*, **74**, 2224 (1970).

(15) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 42.

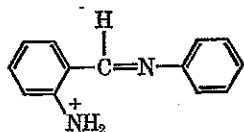
(16) E. Fisher and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).

(17) See P. DeMayo and S. T. Reid, *Quart. Rev.*, **16**, 393 (1961).

470-nm band to the protonated form of IV since a



similar band was produced in sulfuric acid, and (b) the 620 nm, which is also produced in a rigid glass, to the cation



Similar bands have been observed from some aromatic amine cations.¹⁸

Various possible mechanisms which account for the photochromic effect observed for *o*-hydroxyanils in various polar and nonpolar solvents have been recently summarized.⁸ The work presented above shows that the photochromic band may arise from an *ortho* group other than *o*-OH, provided that this group is capable of transferring a hydrogen atom to the nitrogen of the $>\text{C}=\text{N}-$ group. It should be recognized that at this stage the geometric isomer (quinoid form) is still not precisely defined. Further investigations of some benzylideneanilines and salicylideneanilines are in progress.

(18) G. N. Lewis and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 2801 (1942); T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).